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Crystal Phase Study of Pigment Red 254 in the Presence of Ionic Liquids

S. S. Shamekhi[1], F. Nourmohammadian[2*]

[1]. M. Sc., Department of Organic Colorants, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran.

[2]. Associate Professor, (a) Center of Excellence for Color Science and Technology and (b) Department of Organic Colorants, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran.

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ABSTRACT

Polymorphism is difined as different crystalline phases with the same chemical structure. Diketopyrrolopyrrole (DPP) derivatives, as the innovative heterocyclic pigments, follow this pattern and most of times exist in two crystalline forms of alpha and beta with various application in different industries. Herein, synthesis of 3, 6-Bis (4-chlorophenyl) -2, 5-dihydropyrrolo [3,4-c] pyrrole-1,4-dione called Pigment Red 254 (PR 254) with selected crystalline phase using ionic liquids was achieved without any further need to conventional methods for crystalline phase separation after synthesis. Observed different physical properties such as melting points and color properties of the obtained pigment (PR 254 in α and β crystalline phases) are clarified.Prog. Color Colorants Coat. 5(2012), 1-6. © Institute for Color Science and Technology.

1. Introduction

Diketopyrrolopyrrole (DPP) derivatives, as high-performance heterocyclic pigments, have been traditionally used in coloring of fibers, plastics [1, 2, 3] as well as surface and automotive coatings [1, 3], and recently have gained much attention in synthesis of polymers for light-emitting diodes (LEDs) [4, 5], color filters [6, 7], near infrared dyes (NIR Days) [7].

Application of pigments in different industries are depend on their physical crystals and etc. [8]. Each of the crystalline phases properties such as morphologies, crystal modification, size of have different physical properties such as solubility, melting point, density, hardness, crystal shape, optical and electrical properties. Such systems provide an opportunity to determine the application of the pigments in different industries [9, 10, 11, 12].

Diketopyrrolopyrroles are polymorphous and have different crystalline phases as alpha and beta in their powders. Diketopyrrolopyrrole pigments of alpha crystalline phase have good dispensability and can be used as color filters in colored liquids crystal devices (LCDs) [13, 14] and cosmetics [9]. DPPs in alpha phase have been conventionally used as red filters because of their satisfying lightness, excellent light fastness and good heat resistance . Nowadays, they are also used in colored polymers for LEDs [10]. The beta-modification is used as the form of powder and pastes useing in printings, Inks and also is suitable for coloring of high

*Corresponding author: nour@icrc.ac.ir

molecular weight organic materials [13, 14]. Although phase separation as an additional step after synthesis is time and energy consuming and also an expensive level, but is needed for final application of these pigments [13, 15].

3,6-Bis (4-chlorophenyl)-2,5-dihydropyrrolo [3,4-c] pyrrole-1,4-dione, Pigment Red 254, one of the most famous pigments in this family, exists in two forms of α and β crystalline phases (α-PR 254 and β-PR 254) [9,10]; which can be observed with X-ray diffraction (XRD) method. Alpha and beta crystalline phases have their specific XRD patterns [10, 12, 13].

This work is related to analysis of the ionic liquid performance on phase separation of the pigment crystalline phases during the synthesis by temperature controlling. The neutral counter ion of BF_4^- and a cation based on di-alkyl- imidazolium are selected, since this kind of ionic liquid is stable under alkaline reaction conditions [16, 17].

2. Experimental

2.1. Materials

The chemicals were purchased from Merck (Germany) and Fluka Chemical Company (BuchsSwitzerland) and used without further purification. Ionic liquids and *t*-amyl-ONa were synthesized according to references of [15, 1] respectively.

2.2. Measurements

Melting point is determined using a Perkin Elmer Pyris 6 differential scanning calorimeter (DSC). The UV-Vis spectrum of the pigment is measured using a Cecil 9200 double beam spectrophotometer in $CHCl_3$.

IR spectra are measured on a Perkin-Elmer Spectrum One BX Fourier transform FT-IR spectrophotometer. ^{1}HNMR spectrum was recorded on a BRUKER DRX-500 AVANCE spectrometer at 500.13. NMR spectra were obtained from solutions in DMSO-d_6. Crystal phases were detected by X-ray diffraction (XRD) patterns on a Philips-PW3040/60 X-ray diffract meter with Kα radiation.

2.3. Synthesis

2.3.1. Synthesis of the pigment in ionic liquids via succinate route

p-Chlorobenzonitrile (2.65 g, 20 mmol) was added to sodium t-amyl oxide (5 mL) in a four-necked flask equipped with a stirrer, thermometer and a reflux condenser tube. After five minutes, ionic liquid (0.5 ml) and diethyl succinate (2 mL, 10 mmol) was added to the reaction mixture. The mixture was stirred overnight at 30˚C. The highly viscose precipitated pigment was diluted using 20 ml water and filtrated. The filtered cake was rinsed by methanol to remove the remained ionic liquid and then dried at 80 ˚C in vacuum.

2.3.2. Analytical data of the synthesized pigment

3, 6- Bis (4-chlorophenyl) -2, 5- dihydropyrrolo [3, 4-c] pyrrole-1,4-dione (pigment red 254):

Red powder; m.p. > 300˚C; IR (KBr) (ν_{max} cm^{-1}): 3436 (NH); 2931(CH); 1635 (C=O); 1392, 1169(C-N); λ_{max}/nm (DMSO) 520, 482;^{1}H NMR (500 MHz, DMSO-d_6):δ_H 7.65 (4H, d, J_{HH} 13.3 Hz, 4CH), 7.87 (4H, d, J_{HH} 13.3 Hz, 4 CH) (Figure 1).

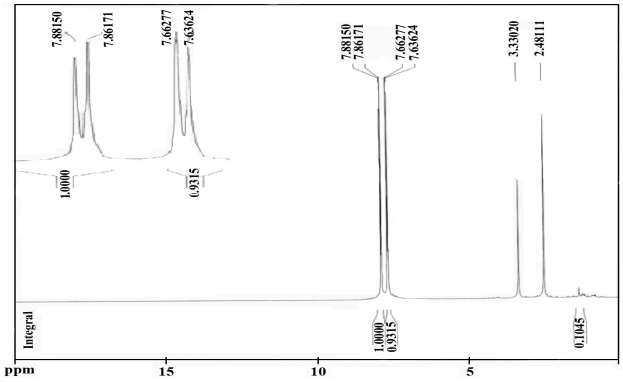


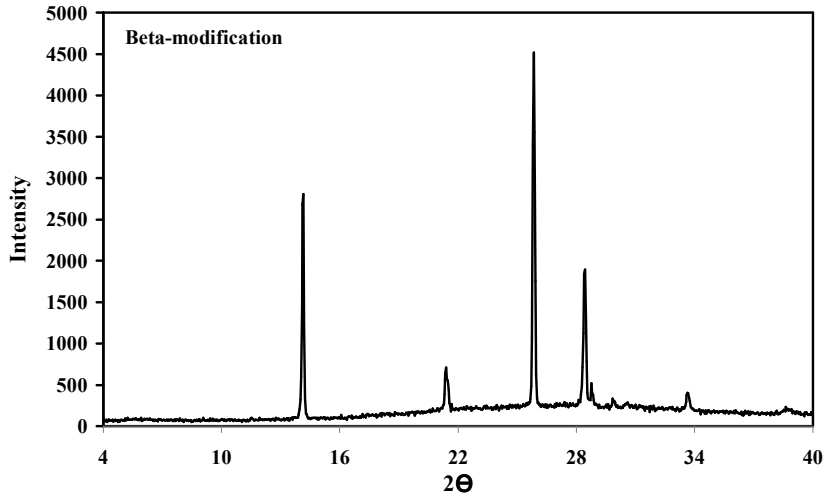
Figure 1: ^{1}HNMR spectra of the synthesized 1, 4-di-chloro-diketopyrrolopyrrole.

3. Result and discussion

In spite of mixed crystalline phases of alpha and beta in Cl-DPP powder after synthesis via conventional methods at 100-110˚C [1, 3, 18], pure individual crystalline phases can be obtained using ionic liquids as media by controlling the temperature during the synthesis. It should be noted that the synthesis occured in a mild condition (T < 70˚C). Synthesis in 1-hexyl-3-methyl-imidazolium tetrafluorobroate, [HMIM][BF_4], medium is temperature independent and alpha crystalline phase was only obtained.

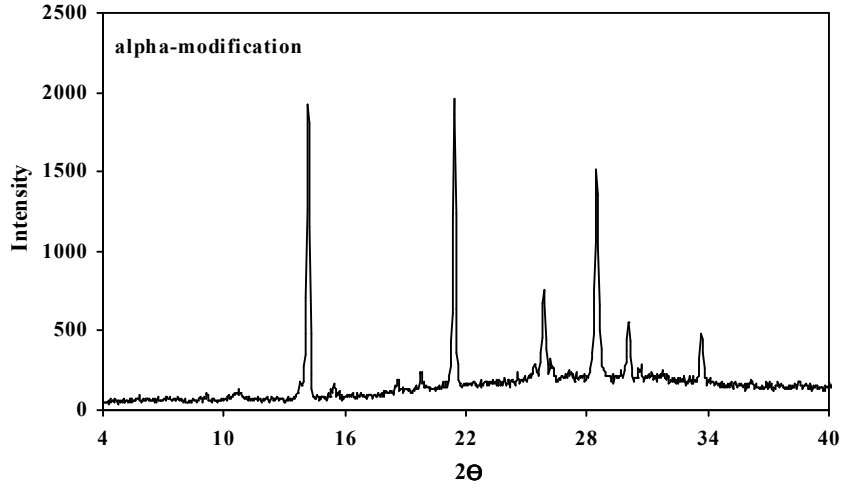
3.1. XRD pattern

The produced pigments which were synthesized at a higher temperatures (50-70˚C), had a darker color and higher melting point in comparison with the pigments produced at lower temperatures (30-50˚C) in 1-butyl-3-methylimidazolium tetrafluorobroate, [BMIM][BF_4]. These differences in physical properties could be considered as crystalline phase separation which has been verified by X-ray diffraction spectroscopy. The XRD patterns of the pigments with pure crystalline phases are shown in Figures 2 and 3.



2θ degree	*d*-value ˚A	Rel. int. %
14.14	6.25	65.9
21.41	4.14	11.4
27.30	**3.13**	**100.0**
28.79	3.09	14.4

Figure 2: XRD spectra of Cl-DPP in β –modification.



2θ degree	*d*-value ˚A	Rel. int. %
14.18	6.24	100.0
21.42	4.14	98.6
25.85	3.44	32.3
28.47	**3.13**	**72.5**
30.06	2.97	21.7
33.68	2.65	17.6

Figure 3: XRD spectra of Cl-DPP in α -modification.

According to [1], the bragg angle (2θ) of 28.1 ± 0.3˚ is a characteristic of α-crystalline phase and the bragg angle (2θ) of 27.0 ± 0.3˚ is a characteristic of *β*-crystalline phase. Peaks with 2θ = 27.30˚ with the intensity of 100% in Figure 2 and peaks with 2θ = 28.47˚ with the intensity of 72.5% in Figure 3 confirm the achievement of pure crystalline phases.

3.2. Melting point and DSC pattern of the pigment

As it is depicted in Figure 4, melting point of the produced pigment is shifted to higher value by changing the medium from [BMIM][BF_4] to [HMIM][BF_4].

The produced pigment in [HMIM][BF_4] have higher melting point value compared to the synthesized pigment in [BMIM][BF_4] at 30˚C. Pigment's color in receiving to their melting point is also different. These differences are pertaining to the separation of crystalline phase which was proved by XRD patterns for Cl-DPP by controlling the reaction media or conditions. The produced pigment in alpha crystalline phase has higher melting point value which is related to its higher thermal stability in relation to the beta-phase, and the obtained pigment in *β*-crystalline phase has lower melting point.

3.3. Effects of ionic liquids on color differences

With a similar counter ion, different length of adjoined-alkyl chain to cation of ionic liquids, the shorter alkyl chain ([BMIM][BF_4]) cause pigment with a lighter color and in contrast, the longer alkyl chained ionic liquids ([HMIM][BF_4]) resulted in a darker color pigments with a same hue. These distinct physical properties of the synthesized pigment in different media arise from their different crystalline natures. Figure 5 shows the pictures of pigment red 254 in two different pure crystalline phases of alpha and beta.

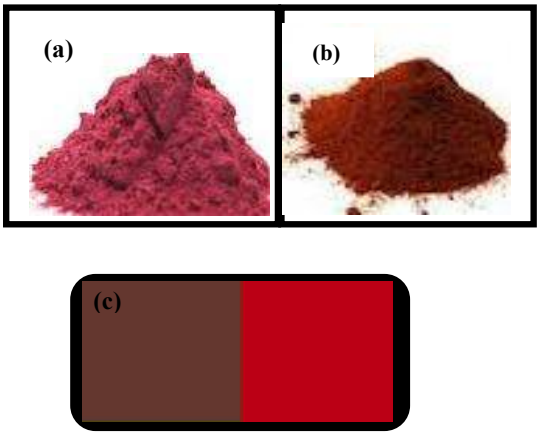


Figure 5: Cl-DPP, synthesized with ionic liquids media: a) alpha phase, medium of [HMIM][BF_4], b) beta phase, medium of [BMIM][BF_4], and (c) differences in shade of pigment by "Chromix color think pro3.0" software with help of their *La*b** data.

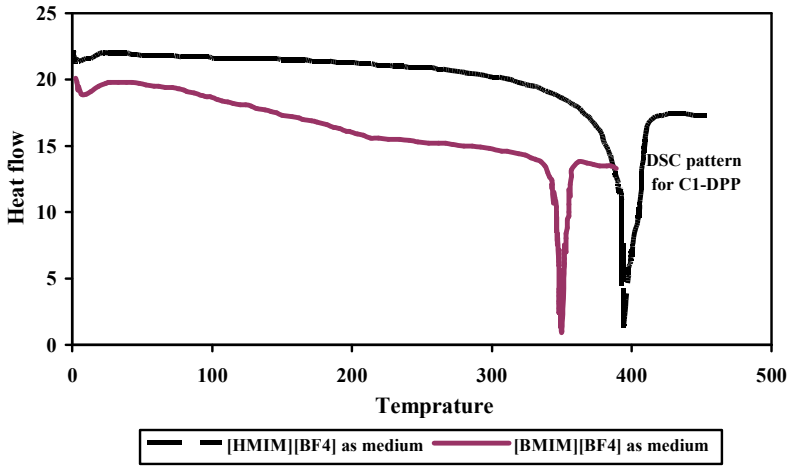


Figure 4: DSC of produced pigments in different crystal phase.

Alpha crystalline phase of the PR 254 has a bluish-red shade while the beta crystalline phase shows more yellowish-red color. In this study, the color differences due to various crystalline phase are explained by "Chromix color think pro3.0" software with using their La*b*data (Figure 5(c))

Color differences of the pigment were measured under different color systems and color sources. The obtained data are revealed in Table 1. Considering Table 1 and comparison of the obtained data, differences in lightness and color between the α-PR 254 and β-PR 254 are apparent and show that β-PR 254 was lighter than α-PR 254.

Two thick disks were made by pressing of the pigment in two crystalline phases and were subject to reflectance spectroscopic studies. The results are shown in Figure 6 along with their *L*a*b** data. Disks are showing different lightness in the *lab* color space as revealed in Figure 6.

4. Conclusions

In conclusion, crystal phase separation of DPPs during the synthesis of these pigments via succinate route in ionic liquids media under solvent free conditions were observed. In this approach, diethyl succinate, a more available and less expensive reagent, was used to produce DPPs while according to references [3, 4], previous approaches with this ester were failed. Ionic liquids not only act as catalyst in the synthesis process but also played their role as a phase dictator by changing the polarity of alkyl chain adjoined to the cation of ionic liquids. DSC patterns show that pure alpha crystalline phase with a bluish-red color have a higher melting point value and and also superior thermal stability.

Table 1: Color difference of synthesized Cl-DPP pigments in two crystalline phase under Lch and Lab color systems.

Pigment	Sources	L	C	h	a*	b*
α-PR 254	A	31.35	9.34	73.08	2.718	9
	TL84	32.26	11.17	63.9	4.917	10.03
	D65	**31.908**	**10.467**	**80**	**1.817**	**10.308**
β-PR 254	A	31.69	8.22	35	6.74	4.72
	TL84	32.84	10.79	38.24	8.48	6.68
	D65	**32.08**	**7.82**	**43.60**	**5.66**	**5.5**

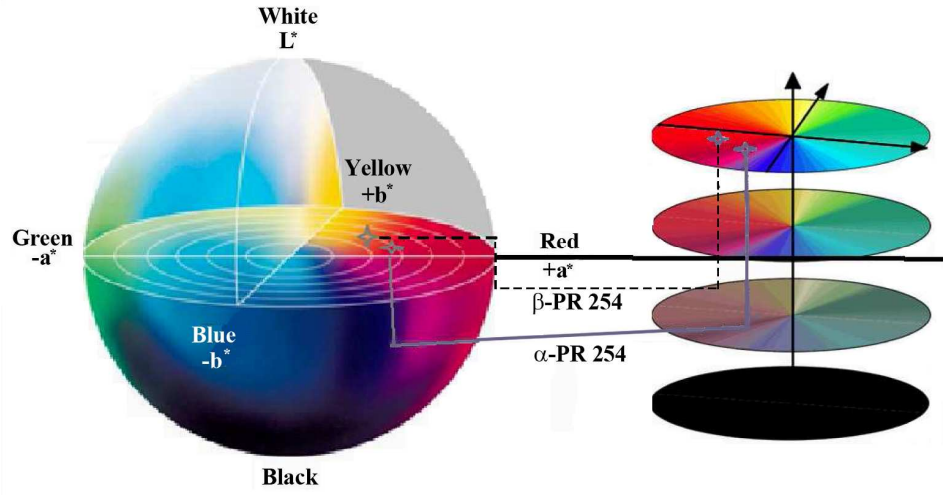


Figure 6: Color difference of the synthesized α-PR 254 and β-PR 254 under Lab color systems.

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